



Electrochemical investigation of the adsorption behaviour of anhydrides and imides on iron in acid medium

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Abstract

The capacitance method was applied to the study of the adsorption of anhydrides and imides with different size of the anhydride and imide ring on iron electrodes in acid medium. It was found that the addition of anhydrides and imides to sulphuric acid solution leads to a decrease in the electrode double layer capacitance. The latter is determined by the adsorption of the compounds investigated. Verifying the validity of Frumkin's isotherm adsorption parameters which characterize the interaction forces between the species in the adsorbed layer, their maximum surface excess, as well as the area occupied by a single adsorbate, were determined. The data obtained, and those provided by quantum-chemical calculations of the partial electron charges and the geometric area of the organic molecules studied, form the basis of a discussion on the orientation of the species adsorbed. The inhibiting effect observed is explained in relation to the adsorption behaviour.

1. Introduction

The inhibiting effect of organic compounds on metal corrosion in an aggressive medium is determined by their adsorbability at the electrode–electrolyte interface [1–7]. Based on the information concerning the degree of surface coverage by organic molecules, the orientation of these molecules, and the variation of adsorption characteristics with the electrode potential, a correlation between the adsorption and kinetic dependencies can be derived and the mechanism of the organic substance on the rate of the electrode process can be developed. The adsorption processes taking place at the electrode–electrolyte interface depend on the nature of both the electrode and the organic substance (i.e., the structure), the presence of functional groups and the electron density distribution in the molecule of the organic substance are factors to be accounted for.

The present work examines the adsorption of anhydrides and imides with different size of the corresponding ring at the iron/sulphuric acid solution interface with a view to their application as inhibitors for iron corrosion. The adsorption behaviour of the examined organic substances on polycrystalline iron electrodes was studied using the capacitance measurement method, which has been successfully used in previous investigations [8–11].

The results obtained are discussed on the grounds of data obtained by quantum chemical calculations of the

structure and the distribution of partial electron charges in the molecules.

2. Experimental details

The electrochemical measurements were carried out in 0.1 M H₂SO₄. The working electrodes were made of Fe of spectral purity (15 ppm impurity level). To achieve a reproducible surface area the following electrode pre-treatment was applied. The electrodes were polished both mechanically and electrochemically, thoroughly washed with doubly distilled water and immersed under current in the cell. They were then subjected to cathodic polarization for an hour at a potential of –0.6 V in H₂SO₄ solution. The solution was saturated with hydrogen prior to the experiment. Thus an electrode of an average roughness factor of 1.66 was obtained. The procedure for roughness factor determination was previously [11] described. All capacitance values were referred to the real electrode surface area. A Pt mesh positioned symmetrically around the working electrode served as a counter electrode. A saturated calomel electrode was used as reference. All potential values cited are referred to the NHE.

The experiments were carried out at 20 °C in a conventional glass cell for impedance measurements. An a.c. P-568 bridge at a frequency of 870 Hz was used. Preliminary investigation [11] showed that the differen-

tial capacitance of the iron electrodes was practically independent of the perturbation frequency for frequencies above 800 Hz.

The potential range studied was rather narrow, this being determined by the fact that at potential values, E , more negative than -0.6 V hydrogen was evolved, while at potentials more positive than -0.25 V the iron started to passivate [12].

The organic substances studied were synthesized in house. Their purity was controlled by TLC and infrared-spectroscopy. To increase their solubility, they were introduced as ethanol solutions of a concentration of 2 vol%. The concentration of the organic substances varied in the range $0.05\text{--}5\ \mu\text{mol dm}^{-3}$. The solutions were deaerated by purified hydrogen.

The MNDO method [13] was applied to provide the values of atomic residual charges in the molecules, the length of the valence bonds, the dihedral torsion angles, the energy of the highest occupied molecular orbital etc.

3. Results

3.1. Quantum chemical calculations

The quantum chemical calculations provided information regarding partial charges, localized in the anhydride, imide and benzene rings. The geometric areas of the different rings and of the molecules were also determined. In calculation of the areas of diphenyl anhydride and diphenimide, it is important to take account of the fact that the benzene residues and the seven-atom anhydride and imide ring, respectively, do not lie in one and the same plane. It is known from the

literature [14] that anhydrides and imides protonate in an acid medium. The quantum chemical calculations carried out show also that a hydrogen cation from the solution is bonded to the O- and N-atom in the anhydride and imide ring, respectively.

The structural formula and the distribution of partial charges in the molecules of protonated anhydrides and imides are presented in Figures 1 and 2, correspondingly. From the data on the electron density of the organic substances studied it can be concluded: (i) that a partial positive charge (δ^+) is localized in the anhydride and imide rings. It is greatest in maleic anhydride and maleinimide. The transition from maleic to phthalic anhydride and the increase of the ring size produce a decrease in δ^+ ; (ii) that a partial negative charge (δ^-) is localized in the benzene residues, which increases with increase in the size of the anhydride and the imide ring; (iii) that there is δ^- at the oxygen atoms in the carbonyl groups, which is smallest in maleic anhydride and maleinimide and greatest in naphthalic anhydride and naphthalimide; and (iv) that naphthalimide differs from the rest of the investigated substances because both partial charges (δ^+ and δ^-) localized in the imide- and in the naphthal rings are commensurate.

The values of the energy in the highest occupied molecular orbital, E_{HOMO} , obtained in this study, are presented in Table 1 for the anhydrides and in Table 2 for the imides studied.

3.2. Electrochemical measurements

The differential capacitance against potential dependencies for iron electrodes in aqueous ethanol solutions of 0.1 M H_2SO_4 with and without the addition of maleic,

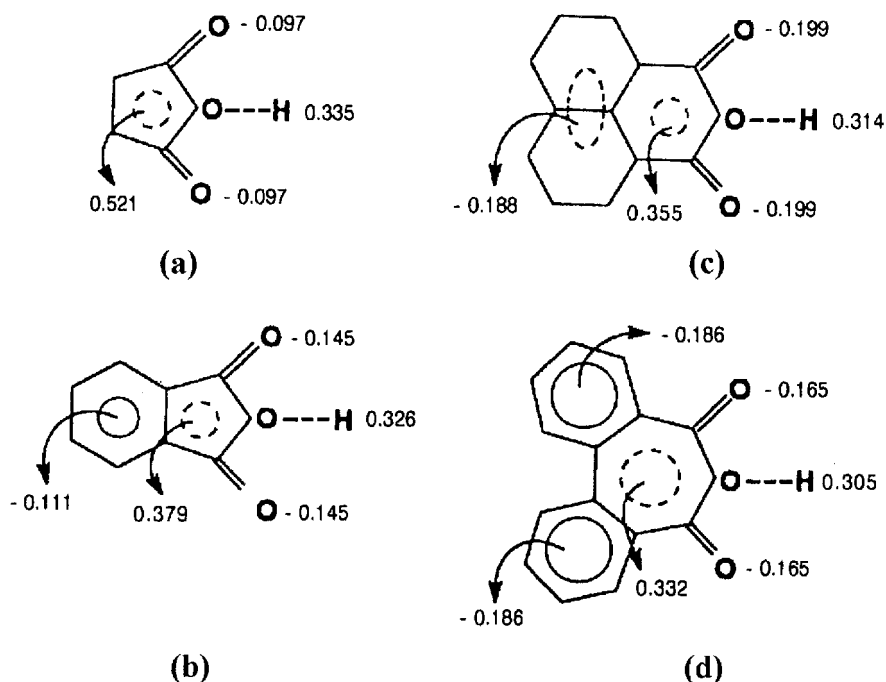


Fig. 1. Molecular structure and distribution of partial charges in the protonated molecules of: (a) maleic anhydride, (b) phthalic anhydride, (c) naphthalic anhydride and (d) diphenyl anhydride.

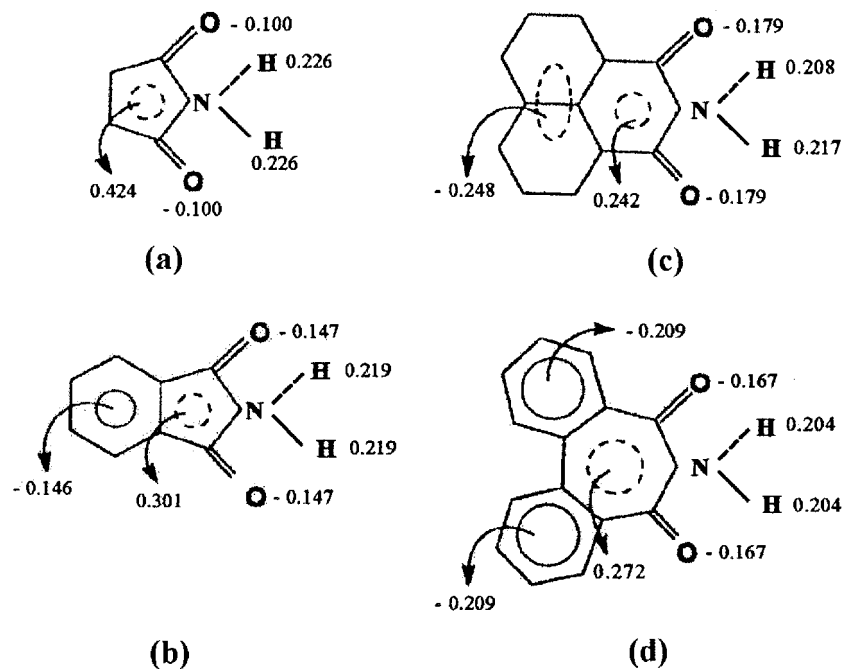


Fig. 2. Molecular structure and distribution of partial charges in the protonated molecules of: (a) maleinimide, (b) phthalimide, (c) naphthalimide and (d) diphenimide.

Table 1. Quantum chemical data for E_{HOMO} and values of the parameters characterizing the adsorption of anhydrides with different ring size on iron electrode in 0.1 M H_2SO_4

Anhydride	$-E_{\text{HOMO}}$ /eV	a	$10^{-6} B$ /dm ³ mol ⁻¹	$-\Delta G_A$ /kJ mol ⁻¹	$10^{10} \Gamma_{\text{max},1}$ /mol cm ⁻²	S_1 /nm ²	$10^{10} \Gamma_{\text{max},2}$ /mol cm ⁻²	S_2 /nm ²
Maleic	16.7782	-0.27	4.01	46.85	1.86	0.89	—	—
Phthalic	14.6086	-0.38	3.85	46.75	1.58	1.05	—	—
Naphthalic	13.2456	-0.50	3.60	46.58	2.16	0.77	—	—
Diphenyl	13.0548	-0.45	3.73	46.67	2.62	0.63	1.94	0.85

phthalic, naphthalic and diphenyl anhydride are plotted in Figure 3(a), (b), (c) and (d), respectively. Figure 4(a–d) presents the analogous dependencies for malein-, phthal-, naphthal- and diphenimide.

The comparison of curves 1 and 1' in Figures 3 and 4 shows that the addition of ethanol to H_2SO_4 -solution slightly changes the capacitance of the iron electrode in the cathodic branch. The addition of anhydrides and imides investigated to the blank solution affects the character of C/E curves, as well as the values of the iron electrode capacitance. The latter decreases with increase in concentration.

Comparison of the C/E curves in Figures 3(a–d) and 4(a–d) suggests that:

- The relative decrease in the capacitance which is connected with the adsorbability of the compounds is commensurate for the investigated anhydrides and imides of different ring size.
- Wide capacitance minimum, shifted in the negative direction, is observed in the presence of the basic compounds maleic anhydride (Figure 3(a)) and maleinimide (Figure 4(a)). This shift is assumed to be connected with the presence of a single adsorption center, in this case (the anhydride and imide ring), where δ^+ is localized.
- A shift in negative direction of the capacitance minimum is observed in the presence of phthalic anhydride (Figure 3(b)) and also phthalimide

Table 2. Quantum chemical data for E_{HOMO} and values of the parameters characterizing the adsorption of imides with different ring size on iron electrode in 0.1 M H_2SO_4

Imides	$-E_{\text{HOMO}}$ /eV	a	$10^{-6} B$ /dm ³ mol ⁻¹	$-\Delta G_A$ /kJ mol ⁻¹	$10^{10} \Gamma_{\text{max},1}$ /mol cm ⁻²	S_1 /nm ²	$10^{10} \Gamma_{\text{max},2}$ /mol cm ⁻²	S_2 /nm ²
Maleinimide	16.4521	-0.30	3.90	46.75	1.98	0.84	—	—
Phthalimide	14.3849	-0.40	3.75	46.66	1.65	1.01	—	—
Naphthalimide	13.0765	-0.47	3.63	46.58	2.13	0.78	—	—
Diphenimide	12.9496	-0.45	3.73	46.67	3.40	0.49	1.90	0.87

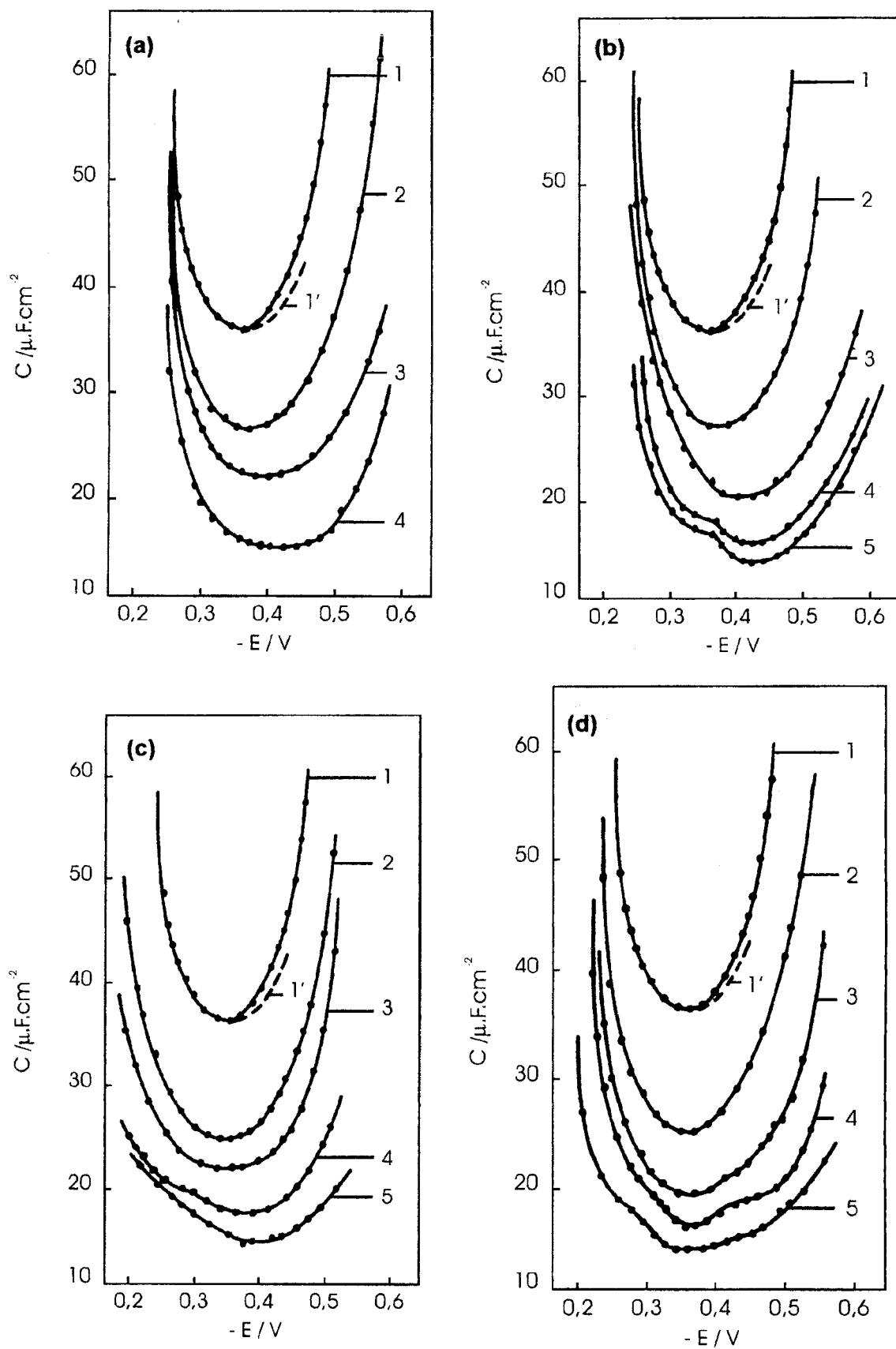


Fig. 3. Capacitance against potential curves for iron in 0.1 M H_2SO_4 (curve 1), in 0.1 M H_2SO_4 with the addition of 2 vol% of $\text{C}_2\text{H}_5\text{OH}$ (curve 1') as well as in the presence of (a) maleic anhydride, (b) phthalic anhydride, (c) naphthalic anhydride and (d) diphenyl anhydride. Concentration values are: (1) 0, (2) -0.25 , (3) -0.50 and (4) $-2.50 \mu\text{mol dm}^{-3}$ (in Figure 3(a)); (1) 0, (2) -0.25 , (3) -0.50 , (4) -1.25 and (5) $-2.50 \mu\text{mol dm}^{-3}$ (in Figure 3(b), (c) and (d), respectively).

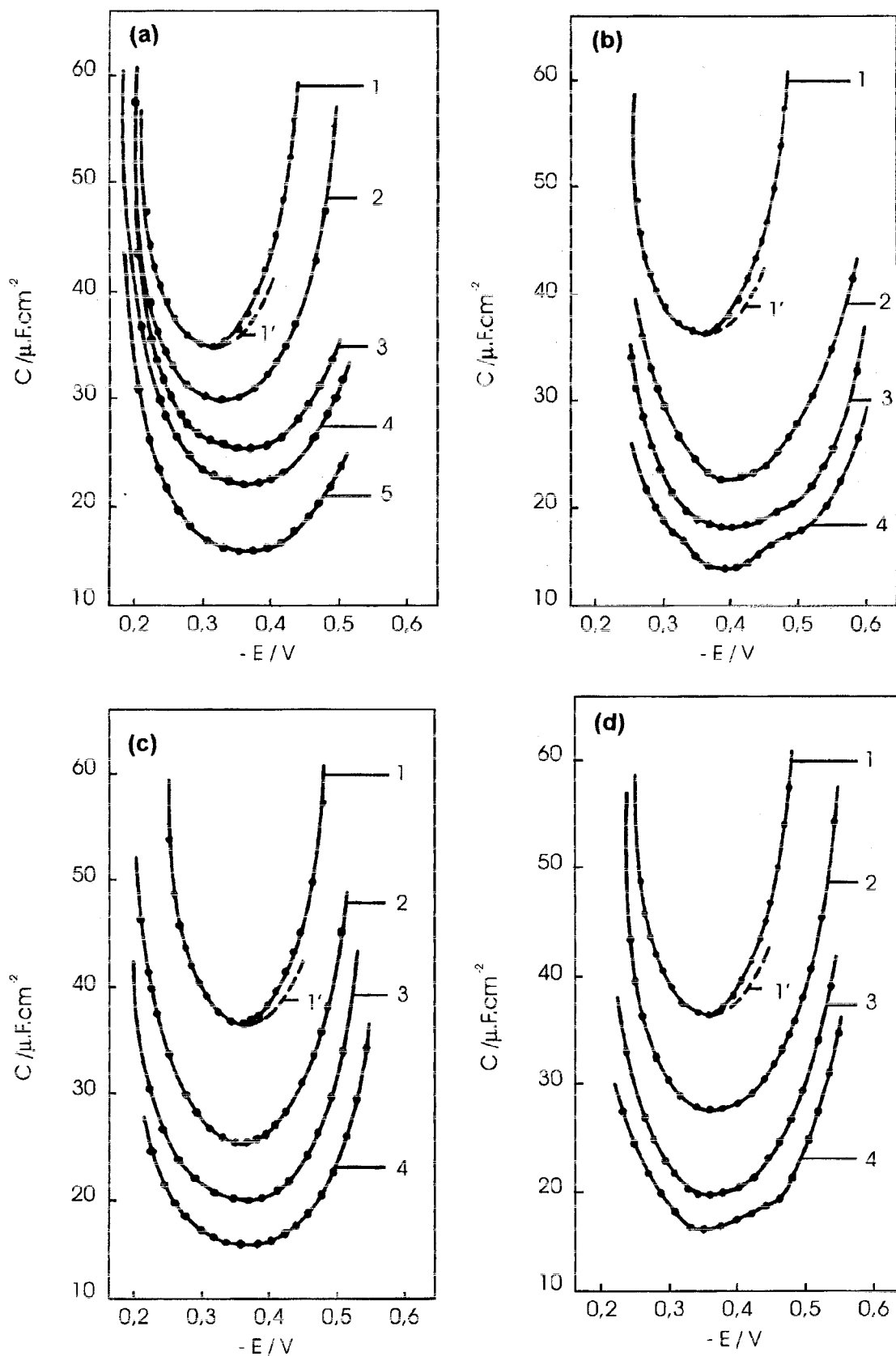


Fig. 4. Capacitance against potential curves for iron in 0.1 M H_2SO_4 (curve 1), in 0.1 M H_2SO_4 with the addition of 2 vol% of $\text{C}_2\text{H}_5\text{OH}$ (curve 1') as well as in the presence of: (a) maleinimide, (b) phthalimide, (c) naphthalimide and (d) diphenimide. Concentration values are: (1) -0 , (2) -0.10 , (3) -0.25 , (4) -0.50 and (5) $-2.50 \mu\text{mol dm}^{-3}$ (in Figure 4(a)); (1) -0 , (2) -0.25 , (3) -0.50 and (4) $-2.50 \mu\text{mol dm}^{-3}$ (in Figure 4(b), (c) and (d), respectively).

(Figure 4(b)). In this case the capacitance shift may be explained by the relatively higher δ^+ localized in the anhydride and imide ring when compared to δ^- in the benzene residues.

- (iv) The capacitance minimum range for naphthalimide (Figure 4(c)) is located symmetrically in respect to that in the supporting electrolyte solution which may result from the identical size of the partial charges (δ^+ and δ^-) localized in the imide and in the naphthalic ring.

It is seen from the capacitance curves presented in Figures 3 and 4 that the adsorption proceeds at potentials which are not in the corrosion potential range (from -0.24 to -0.27 V). This explains the comparatively low inhibiting effect of the studied anhydrides and imides irrespectively of their good adsorbability.

Quantitative evaluation of the organic substance adsorbability on the iron/ H_2SO_4 solution interface can be obtained from the adsorption isotherms which give a correlation between the degree of surface coverage (θ) and the bulk concentrations of the organic substance (c_{or}). The former is calculated using the well known formula:

$$\theta = \frac{C_0 - C}{C_0 - C'} \quad (1)$$

where C_0 is the capacitance minimum for iron in the blank solution and C is the capacitance minimum for a definite bulk concentration of the surfactant; C' is the capacitance for $\theta = 1$. C' was estimated from the cross point of the anodic and cathodic linear branches of $1/C$ against $1/E$ relationship for the maximum additive concentration.

The dependencies of degree of coverage against concentration for maleic and naphthalic anhydride are shown in Figure 5. It follows from curves 1 and 2 that maximum values of θ are reached at identical bulk concentration. The θ/c_{or} dependencies obtained for the rest of the studied compounds are not shown in Figure 5. They have a form similar to that of curves 1 and 2, that is, the maximum values of θ are very close to those of maleic and naphthalic anhydride. It is found as well that the maximum values of θ are obtained at identical bulk concentration in case of all compounds ($c_{\text{or}} = 2.5 \mu\text{mol dm}^{-3}$). This verifies the conclusion made that the adsorbability of the organic substances studied is commensurate.

A criterion offered by Damaskin [15] is used to determine the validity of isotherm describing the adsorption process. Following the procedure presented in [15], which is based on the width of the curve $\partial \ln c_{\text{or}} / \partial \theta$ against θ and on the position of the curve's minimum at $\theta = 0.5$. It is concluded that Frumkin's isotherm,

$$Bc_{\text{or}} = \frac{\theta}{1-\theta} \exp(-2a\theta) \quad (2)$$

describes the adsorption process. In Equation 2, B is the adsorption equilibrium constant and a is the attraction

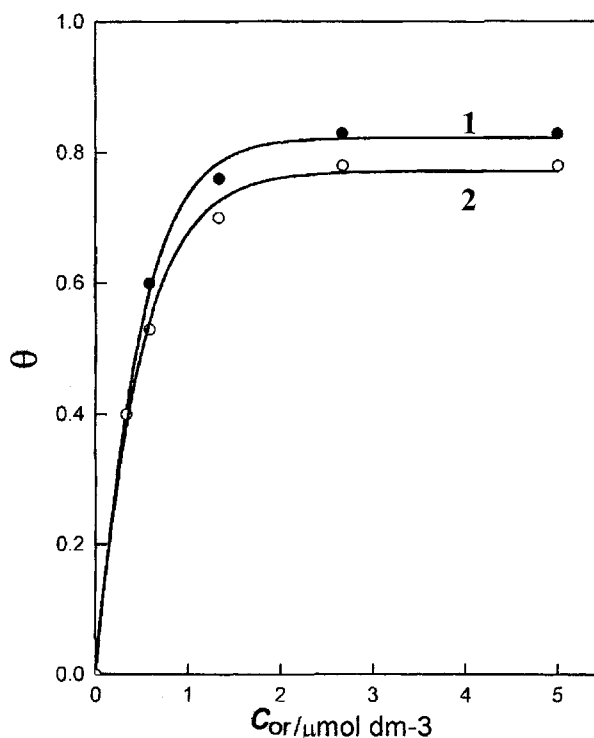


Fig. 5. Surface coverage against additive concentration for (1) maleic anhydride and (2) naphthalic anhydride.

constant characterizing the lateral forces of interaction between the species in the adsorbed layer.

The validity of Frumkin's isotherm, which requires a linear character of the dependencies $\ln[\theta/(1-\theta)c_{\text{or}}]$ against θ , is illustrated for maleic anhydride (line 1) and naphthalic anhydride (line 2) in Figure 6. The values of the correlation coefficient in both cases are 0.988 and 0.992, respectively.

With the aim of attaining more accurate determination of the attraction constant a , an algorithm offered by Damaskin et al. [16] is applied. The latter requires an introduction of a relative concentration $y = c/c_{\theta=0.5}$. The value of $c_{\theta=0.5}$ is obtained from the plot of θ against c_{or} (Figure 5). For $\theta = 0.5$ Frumkin's isotherm is simplified to

$$Bc_{\theta=0.5} = \exp(-a) \quad (3)$$

The ratio of Equation 2 and Equation 3 gives the following expression for y :

$$y = \frac{\theta}{1-\theta} \exp[a(1-2\theta)] \quad (4)$$

Equation 4 is solved to give for a :

$$a = \frac{1}{1-2\theta} \ln \left[\frac{y(1-\theta)}{\theta} \right] \quad (5)$$

The values of a are calculated using a numerical iteration method, that is, θ - y curves are calculated and that which is the best fit of the experimental θ - y dependence provides the value of a . The values of a

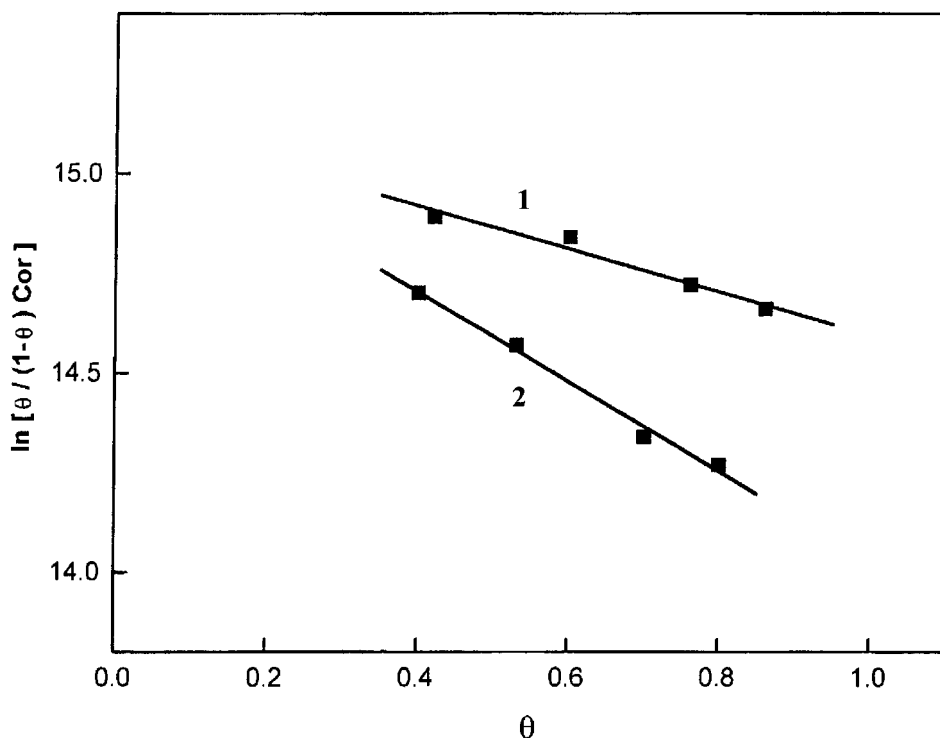


Fig. 6. Dependence of $\ln [\theta / (1 - \theta) c_{or}]$ on θ corresponding to Frumkin's isotherm describing adsorption in 0.1 M H_2SO_4 of (1) maleic anhydride and (2) naphthalic anhydride.

obtained in this study are summarized in Tables 1 and 2 for the anhydrides and imides, respectively. The negative values obtained for all compounds studied indicate the presence of repulsive forces between the adsorbed species.

The equilibrium constant B is estimated from the ratio:

$$B = \frac{\exp(-a)}{c_{\theta=0.5}} \quad (6)$$

It is connected with the energy of adsorption ($-\Delta G_A$) through

$$B = \frac{1}{55.5} \exp\left(\frac{-\Delta G_A}{RT}\right) \quad (7)$$

The values of B and ($-\Delta G_A$) obtained from Equations 6 and 7 are presented in Tables 1 and 2. The comparison of the values of B and of ($-\Delta G_A$) supports the conclusion made, that the adsorption of the different anhydrides and imides at the Fe/H_2SO_4 solution interface is commensurate.

When the adsorption process is realized so that the electrode charge is a function of the electrode potential and degree of surface coverage, that is, $q = q(E, \theta)$, and adsorption equilibrium is established at each potential value, Frumkin's adsorption isotherm is presented in the form [17]:

$$B = B_{\max} \exp[-b(E - E_{\max})^2] \quad (8)$$

where $B_{\max} = B$ at $E = E_{\max}$ (E_{\max} is the potential of maximum adsorption).

The substitution of B in Equation 2 with B from Equation 8 gives for Frumkin's isotherm:

$$B_{\max} c_{or} \exp[-b(E - E_{\max})^2] = \frac{\theta}{1 - \theta} \exp(-2a\theta) \quad (9)$$

The equation obtained gives a relation between the degree of surface coverage (θ) and the electrode potential (E) at a definite concentration of the organic substance (c_{or}).

For maximum concentration of the organic additive ($c_{or, \max}$), which corresponds to a maximum value of θ , Equation 9 is written as

$$B_{\max} c_{or, \max} \exp[-b(E - E_{\max})^2] = \frac{\theta}{1 - \theta} \exp(-2a\theta) \quad (10)$$

whose logarithmic form is

$$\ln\left(\frac{\theta}{1 - \theta}\right) - 2a\theta = \ln[B_{\max} c_{or, \max}] - b(E - E_{\max})^2 \quad (11)$$

The C/E dependencies obtained at the additive maximum concentration lead to linear plots in $\{\ln[\theta / (1 - \theta)] - 2a\theta\}$ against $(E - E_{\max})^2$ whose slope is b . This is illustrated in Figures 7 and 8.

Hence, the maximum surface excess (Γ_{\max}) and the area (S) occupied by an adsorbed molecule can be calculated from Equations 12 and 13, respectively:

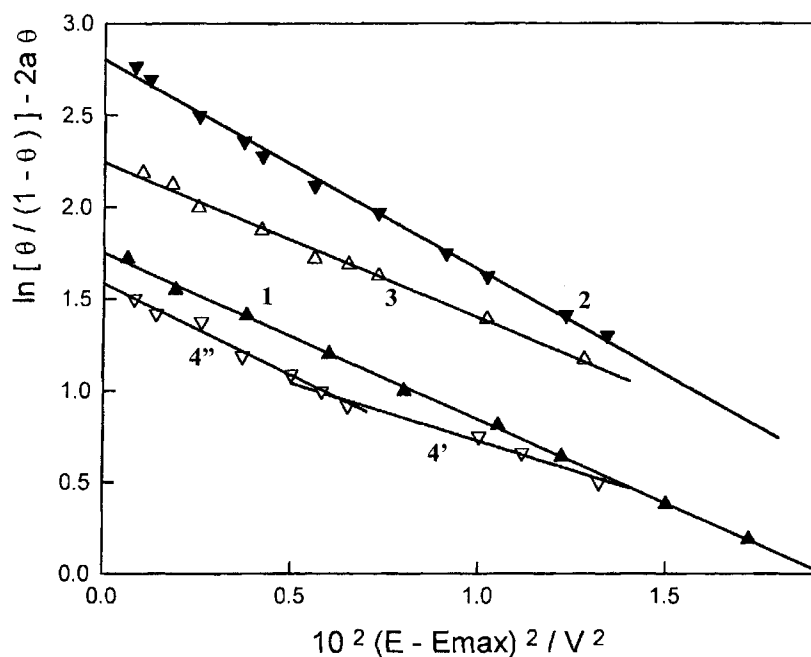


Fig. 7. Dependence of $\{\ln[\theta/(1-\theta)] - 2a\theta\}$ on $(E - E_{\max})^2$ obtained in 0.1 M H_2SO_4 solution of (1) maleic anhydride, (2) phthalic anhydride, (3) naphthalic anhydride and (4' and 4'') diphenyl anhydride.

$$\Gamma_{\max} = \frac{10^{-6}(C_o - C')}{RTb} \quad (12)$$

$$S = 1/\Gamma_{\max}N_A \quad (13)$$

diphenimide by two adsorption states (lines 4' and 4''). The calculated values of Γ_{\max} and S are shown in Tables 1 and 2.

The dependencies presented in Figures 7 and 8 show that the adsorption of maleic, phthalic and naphthalic anhydride and the corresponding imides (malein-, phthal- and naphthalimide) is characterized by a single state (lines 1, 2 and 3), while that of diphenyl anhydride and

4. Discussion

The adsorption behaviour of the anhydrides and imides investigated can be qualitatively and quantitatively interpreted on the ground of the determined values of

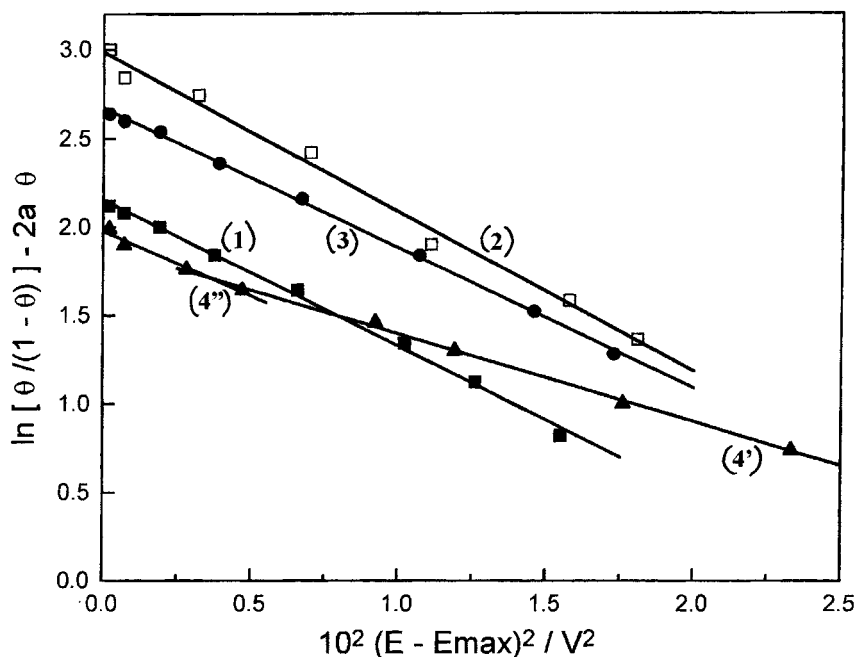


Fig. 8. Dependence of $\{\ln[\theta/(1-\theta)] - 2a\theta\}$ on $(E - E_{\max})^2$ obtained in 0.1 M H_2SO_4 solution of (1) maleinimide, (2) phthalimide, (3) naphthalimide and (4' and 4'') diphenimide.

adsorption parameters B , a , Γ_{\max} and S . Comparing the latter with the data provided by quantum chemical calculations regarding the molecules' geometry and the partial charges distribution, a hypothesis concerning the most probable orientation of the molecules adsorbing at the electrode surface can be advanced.

When the data is interpreted, it should be taken into account that, according to literature data [18], maleinimide and protonated maleic anhydride form dimers in an aqueous solution. In fact, the areas of the adsorbed molecules of these compounds (Tables 1 and 2) are in full agreement with this finding. In dimer formation (Figures 9(a) and 10(a)) the negative charge at one of the oxygen atoms is completely compensated. This leads to smaller repulsion forces between the adsorbed molecules. The smaller negative values of a may be attributed to this, as well as to the lower values of δ^- at the oxygen atoms in the carbonyl groups.

Formation of dimers in the case of protonated phthalic anhydride and phthalimide (Figures 9(b) and 10(b)) is also possible, although there are no literature data. The areas of the adsorbed molecules of phthalic anhydride and phthalimide are 1.08 (nm)^2 and 1.01 (nm)^2 , respectively. They correspond neither to an area of a single

molecule, nor to that of a dimer. Hence, it follows that not all of the molecules of protonated phthalic anhydride and phthalimide form dimers. As the value of S are closer to those of the dimer ($S_{\text{theor.}} = 1.20 \text{ (nm)}^2$), it may be assumed that in this case an equilibrium between single molecules and dimers is reached and it is shifted towards the dimer form.

The negative values of the attraction constant indicate lateral forces of repulsion between the molecules in the adsorbed layer. In the compounds investigated these forces are determined by the presence of symmetrically located charges δ^- at O-atoms of the carbonyl groups. It is known [19] that symmetrically situated functional groups lead to greater repulsion forces when compared to molecules with a single functional group. It is seen from Tables 1 and 2 that the values of a depend directly on the charge δ^- at the oxygen atoms. The repulsion forces grow (a becomes more negative) with the increase of δ^- (Figures 1 and 2).

As has been mentioned, the adsorption of maleic, phthalic and naphthalic anhydride (Figure 7, lines 1, 2 and 3), as well as the corresponding imides (Figure 8, lines 1, 2 and 3), are characterized by a single adsorption state, planar adsorption in this case. The adsorption of

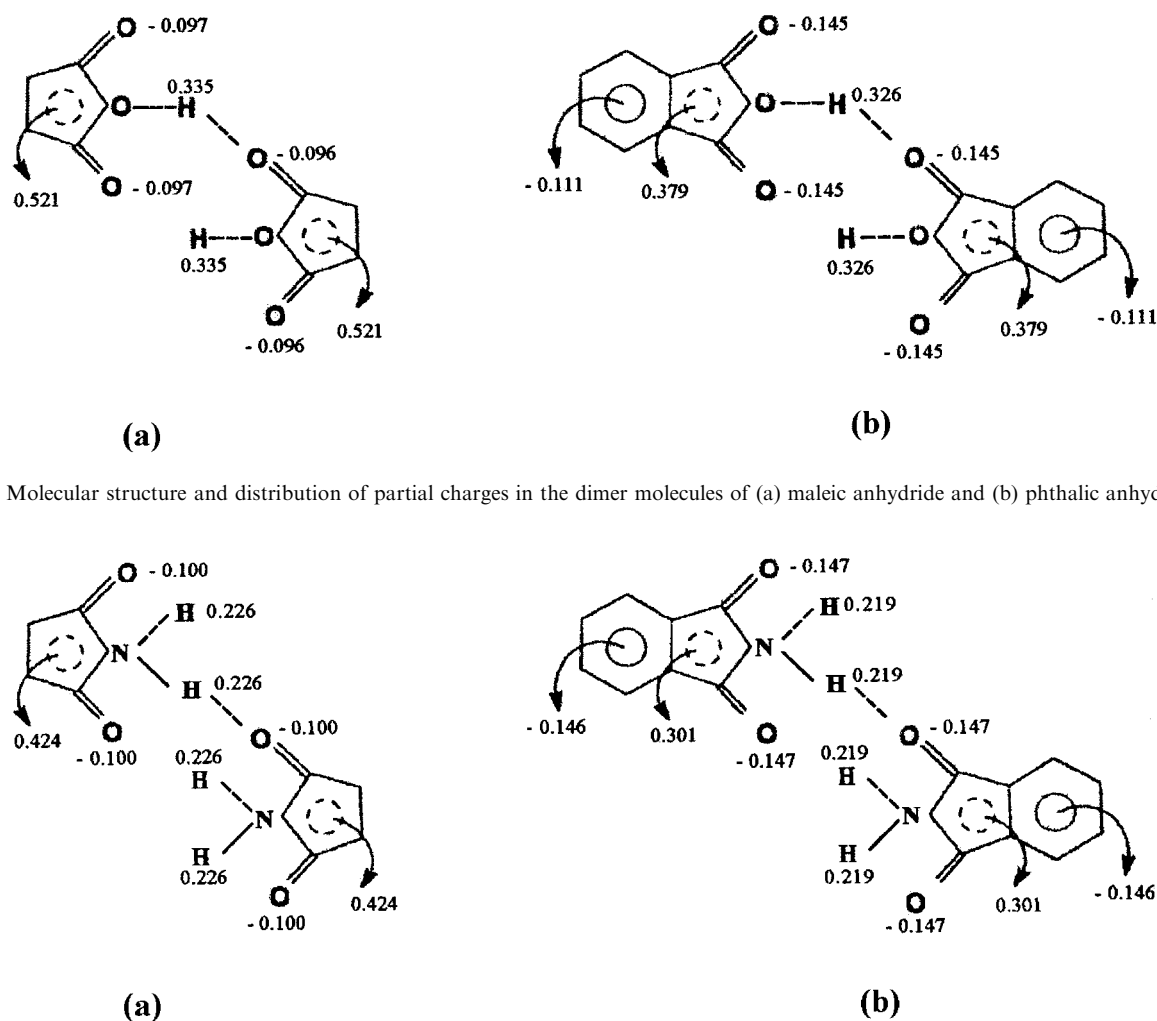


Fig. 9. Molecular structure and distribution of partial charges in the dimer molecules of (a) maleic anhydride and (b) phthalic anhydride.

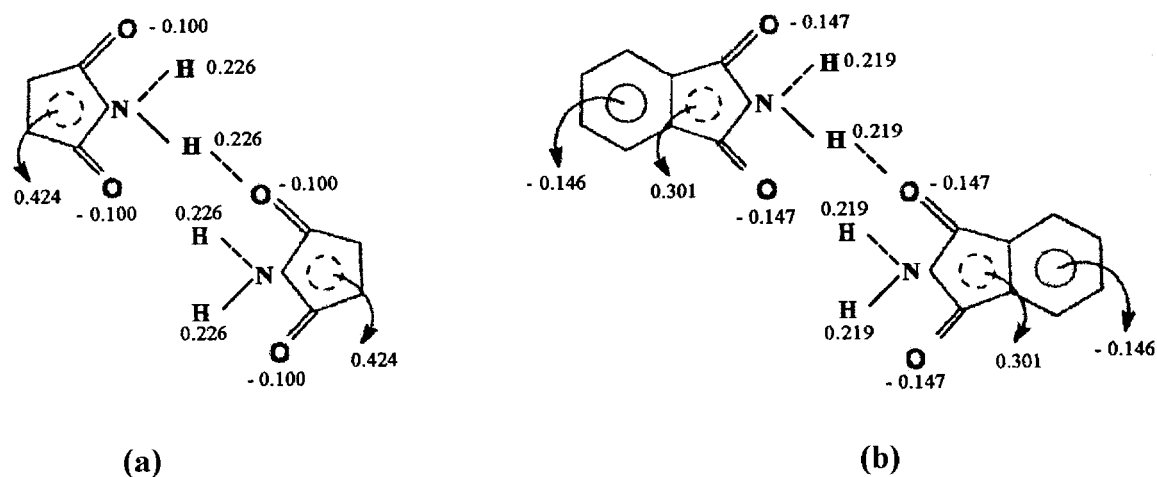


Fig. 10. Molecular structure and distribution of partial charges in the dimer molecules of (a) maleinimide and (b) phthalimide.

diphenyl anhydride and diphenimide is characterized by two adsorption states (Figures 7 and 8, lines 4', and 4''). For diphenyl anhydride both adsorption states are planar. At $E < E_N$ the adsorption is realized through the anhydride ring ($S_1 = 0.63 \text{ (nm)}^2$), while at $E > E_N$ the π -electron interaction leads to adsorption of benzene residues ($S_2 = 0.85 \text{ (nm)}^2$). The assumption of two adsorption states is based on the fact that the seven-atom anhydride ring and the benzene residues do not lie in one and the same plane, as shown by quantum-chemical calculations. The first adsorption state for diphenimide at $E < E_N$ is vertical ($S_1 = 0.49 \text{ (nm)}^2$), while the second one at $E > E_N$ is planar ($S_2 = 0.87 \text{ (nm)}^2$). The vertical orientation in this case is possible because of the presence of a greater total δ^+ at the hydrogen cations (connected to N), when compared to δ^+ localized in the imide ring (Figure 2). The planar orientation is achieved through the benzene residues which, as in case of diphenyl anhydride, do not lie in one and the same plane with the seven-atom imide ring.

The commensurate adsorbability on Fe electrode in sulphuric acid medium of anhydrides and imides could be assumed as resulting from the negligible differences in the values of the electron density as well as in those of E_{HOMO} . According to literature data [1, 4, 20] the inhibiting action (the adsorbability, respectively) of the organic compounds increases with the increase of E_{HOMO} . For the values of B , presented in Tables 1 and 2, an identical tendency is apparent. A deviation is observed in the case of naphthalic anhydride and naphthalimide, which is attributed to the more negative values of a .

5. Conclusions

The electrochemical investigation of the adsorption of anhydrides and imides of different ring size on iron electrodes in sulphuric acid solution provides the following conclusions:

- (i) The adsorbability of the compounds depends on the size and the distribution of the partial charges in the molecules, on the energy of the highest occupied molecular orbital and on the value of the attraction constant.
- (ii) The adsorption proceeds in a potential range, which does not coincide with that of the corrosion potential. The compounds exhibit comparatively poor inhibiting effect.
- (iii) Combining the results derived from capacitance measurements with quantum chemical calculations of the molecular structure of the surfactants and the partial charges, some suggestions concerning the

orientation of the adsorbed species on the metal surface can be made: (a) the adsorption of diphenyl anhydride and diphenimide depends on the potential of Fe electrodes, and (b) the adsorption of maleic, phthalic and naphthalic anhydride as well as that of the corresponding imides (malein-, phthal- and naphthalimide) is characterized by a single adsorption state.

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